UNIVERSITI PUTRA MALAYSIA

CHARACTERISATION OF COPPER (II) OXIDE SYNTHESISED BY PRECIPITATION METHOD

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By

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Chairman: Irmawati Ramli, PhD

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In this study, copper(II) oxide (CuO) nanocrystalline powders were successfully synthesised via precipitation method. The main advantages of the method for the material preparation are the possibility of creating very pure materials and the flexibility of the process with respect to final product quality. Synthesis parameters which were concentration of copper, concentration of precipitating agent, pH and types of precipitating agents were varied and their influence on the microstructural properties of CuO were studied. Results showed that 1.0 M of copper nitrate, $Cu(NO_3)_2$ solution and 1.5 M of ammonium hydroxide, NH_4OH solution were the most suitable molarities for its given the best precipitation yield and improved microstructural properties. The calcination temperature of 623 K was chosen because thermal gravimetric analysis revealed that the precursors fully transformed to CuO at this temperature. As evidenced by X-ray diffraction analysis, all the precursors were in copper hydroxyl nitrate phase and all the calcined samples were pure CuO in 23-36 nm size with monoclinic structure. The FTIR spectra showed the incorporation of nitrate and hydroxide anions into copper cations in the precipitation process. CuO obtained from precipitation at pH 1.6 by using NH_4OH as precipitating

agent showed the higher surface area, 8.7 m^2 g^{-1} in comparison with CuO prepared from ammonium carbonate, $(NH_4)_2CO_3$ and sodium carbonate, Na_2CO_3. For precipitation finished at higher pH, *i.e.* pH 3.0 and pH 4.2, respectively, CuO synthesised from Na_2CO_3 possessed higher surface area in comparison with CuO synthesised from NH_4OH and $(NH_4)_2CO_3$. From electron microscopy studies, tabular crystallites with elongated hexagonal morphology were observed for the CuO prepared by using NH_4OH. CuO precipitated from $(NH_4)_2CO_3$ were in platelet morphology. Granular morphology was observed for the CuO prepared from Na_2CO_3. Results of temperature-programmed reduction in hydrogen showed that the total amount of oxygen removed from CuO was influenced by the surface area of CuO. It was found that higher CuO surface area promised higher reducibility of CuO due to the decreasing of crystallite size.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN KUPRUM(II) OKSIDA MELALUI KAEDAH PEMENDAKAN

Oleh

LAU HOOI HONG

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Pengerusi: Irmawati Ramli, PhD

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Dalam kajian ini, nanokristal serbuk kuprum(II) oksida (CuO) telah berjaya disintesiskan melalui kaedah pemendakan. Kebaikan utama kaedah penyediaan bahan ini adalah mungkin dapat menghasilkan bahan yang sangat tulen dan kefleksibelan proses tersebut berhubung dengan kualiti hasil akhir. Parameter-parameter sintesis seperti kepekatan kuprum, kepekatan agen pemendakan, pH dan jenis agen pemendakan yang berbeza dan pengaruh mereka terhadap ciri-ciri mikrostruktur CuO telah dikaji. Keputusan menunjukkan bahawa 1.0 M larutan kuprum nitrat, $Cu(NO_3)_2$ dan 1.5 M larutan ammonium hidroksida, NH_4OH adalah molariti yang paling sesuai untuk pemberian hasil pemendakan yang paling baik dan memperbaiki ciri-ciri mikrostruktur. Suhu pengkalsinan yang 623 K dipilih kerana analisis terma gravimetri menunjukkan bahawa prekursor-prekursor telah berubah sepenuhnya ke CuO pada suhu tersebut. Seperti yang dibuktikan oleh analisis pembelauan sinar-X, semua prekursor adalah dalam fasa kuprum hidroksi nitrat dan semua sampel yang dikalsinkan adalah fasa CuO yang tulen dalam saiz 23-36 nm dengan struktur monoklinik. Spektra FTIR menunjukkan pergabungan anion-anion nitrat dan hidroksida ke dalam kation-kation kuprum dalam proses pemendakan.

CuO yang terhasil daripada pemendakan pada pH 1.6 dengan menggunakan NH_4OH sebagai agen pemendakan menunjukkan luas permukaan yang lebih besar, 8.7 $m^2\ g^{-1}$ dibanding dengan CuO yang disediakan daripada ammonium karbonat, $(NH_4)_2CO_3$ dan natrium karbonat, Na_2CO_3. Untuk pemendakan yang berakhir pada pH yang lebih tinggi, iaitu pH 3.0 dan pH 4.2, masing-masing, CuO yang disediakan daripada Na_2CO_3 mempunyai luas permukaan yang lebih tinggi dibandingkan CuO yang disintesis daripada NH_4OH dan $(NH_4)_2CO_3$. Daripada kajian mikroskopi elektron, tabular kristal dengan morfologi heksagonal panjang telah diperhatikan untuk CuO yang disediakan dengan menggunakan NH_4OH. CuO yang dimendakkan daripada $(NH_4)_2CO_3$ adalah dalam morfologi platlet. Morfologi granular dapat diperhatikan untuk CuO yang disediakan daripada Na_2CO_3. Keputusan penurunan berprogramkan suhu dalam hidrogen menunjukkan jumlah amaun oksigen yang disingkirkan dari CuO adalah dipengaruhi oleh luas permukaan CuO. Ia adalah didapati bahawa luas permukaan CuO yang lebih tinggi memberikan sifat penurunan CuO yang tinggi disebabkan oleh pengurangan saiz kristal.

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I certify that an Examination Committee met on 30th December 2005 to conduct the final examination of Lau Hooi Hong on her Master of Science thesis entitled "Characterisation of Copper(II) Oxide Synthesised by Precipitation Method" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or currently submitted for any other degree at UPM or other institutions.

LAU HOOI HONG

Date: 12th January 2006

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
DTG	Differential thermal gravimetric
E_r	Reduction activation energy
FHWM	Full width at half maximum
FTIR	Fourier transform infrared
JCPDS	Joint Committee on Powder Diffraction Standards
JEOL	Japan Electron Optics Laboratory
M	Molarity
SEM	Scanning electron microscopy
TCD	Thermal conductivity detector
TGA	Thermal gravimetric analysis
TPR	Temperature-programmed reduction
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Copper(II) Oxide

Copper(II) oxide occurs in nature as the black minerals. It crystallizes in a monoclinic structure. In mineralogy, copper(II) oxide is known as tenorite. Its molecular weight is 79.54 g mol^{-1} and melts at 1603 K. Sometimes, copper(II) oxide is also known as cupric oxide (Richardson, 2003).

Commercially produced copper(II) oxide is usually black, although a brown product (particle size < 1000 nm) can also be produced. Copper(II) oxide is stable to air and moisture at room temperature. It is virtually insoluble in water or alcohols. The oxide dissolves slowly in ammonia solution but quickly in ammonium carbonate solution; it is dissolved by alkali metal cyanides and by strong acid solutions. Hot formic acid and boiling acetic acid solutions readily dissolve the oxide (Richardson, 2003).

Copper(II) oxide is decomposed to copper(I) oxide and oxygen at 1303 K and at atmospheric pressure. The reduction can proceed at lower temperature in a vacuum. Hydrogen and carbon monoxide reduce copper(II) oxide to the copper metal at 523 K and to copper(I) oxide at about 423 K. Ammonia gas reduces copper(II) oxide to copper metal and copper(I) oxide at 698-973 K (Richardson, 2003).

1.2 Structure of Copper(II) Oxide

The structure of copper(II) oxide (4:4 coordination) is unique, and consists of a square planar arrangement of 4 oxygen atoms around each Cu atom, and a tetrahedral arrangement of 4 Cu atoms around each oxygen atom (Figure 1.1). The Cu-O distance is 1.95 Å (Holleman, 2001).

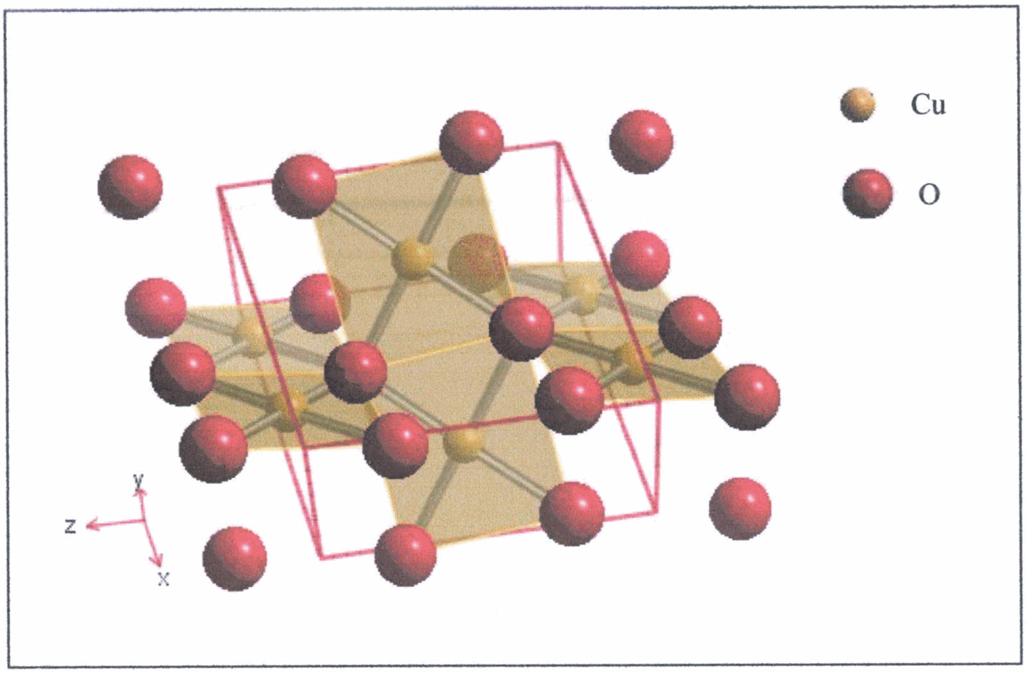

Figure 1.1: Structure of copper(II) oxide.

1.3 Precipitation

Precipitation processes are not only relevant for catalysis, but also for other industries, as for instance the production of pigments (Schüth and Unger, 1997). The aim of this step is to precipitate a solid from a liquid solution. The precipitate is generally a precursor, the nature of which determines the structure and properties of the final solid product (Perego and Villa, 1997; Campanati *et al.*, 2003). Precipitation is one of the most widely employed materials preparation methods especially catalysts and may be used to prepare either single component catalysts and supports or mixed catalysts (Campanati *et al.*, 2003). The main advantages of precipitation for the catalyst preparation are the possibility of creating very pure materials (single phase) and the flexibility of the process with respect to final product quality, *i.e.* small and fine crystallite (Schüth and Unger, 1997).

1.4 Precipitation Parameters

Usually precipitates with specific properties are desired. These properties include the nature of the phase formed, chemical composition, purity, particle size, surface area and pore size, pore volumes, and many more, as well as the requirements of downstream processes like drying, pelltetizing or calcination (Schüth and Unger, 1997; Campanati *et al.*, 2003). Certainly, the yield percentage of precipitation is also important for manufacturer in order to reduce the production cost (Schüth and Unger, 1997).

All process parameters basically influence the quality of the precipitates. Fine tuning of the parameters is necessary in order to produce the required material (Campanati *et al.*, 2003). These parameters are shown in Figure 1.2.

In this work, the influence of concentration of raw materials (copper nitrate and ammonium hydroxide) on the yield and physico-chemical properties of copper(II) oxide was investigated. The purpose is to obtained suitable molarity of these raw materials which to be used in the investigation of pH and precipitating agent on the physico-chemical properties of copper(II) oxide. The details of the effect of these parameters on copper(II) oxide were discussed in Chapter 4.

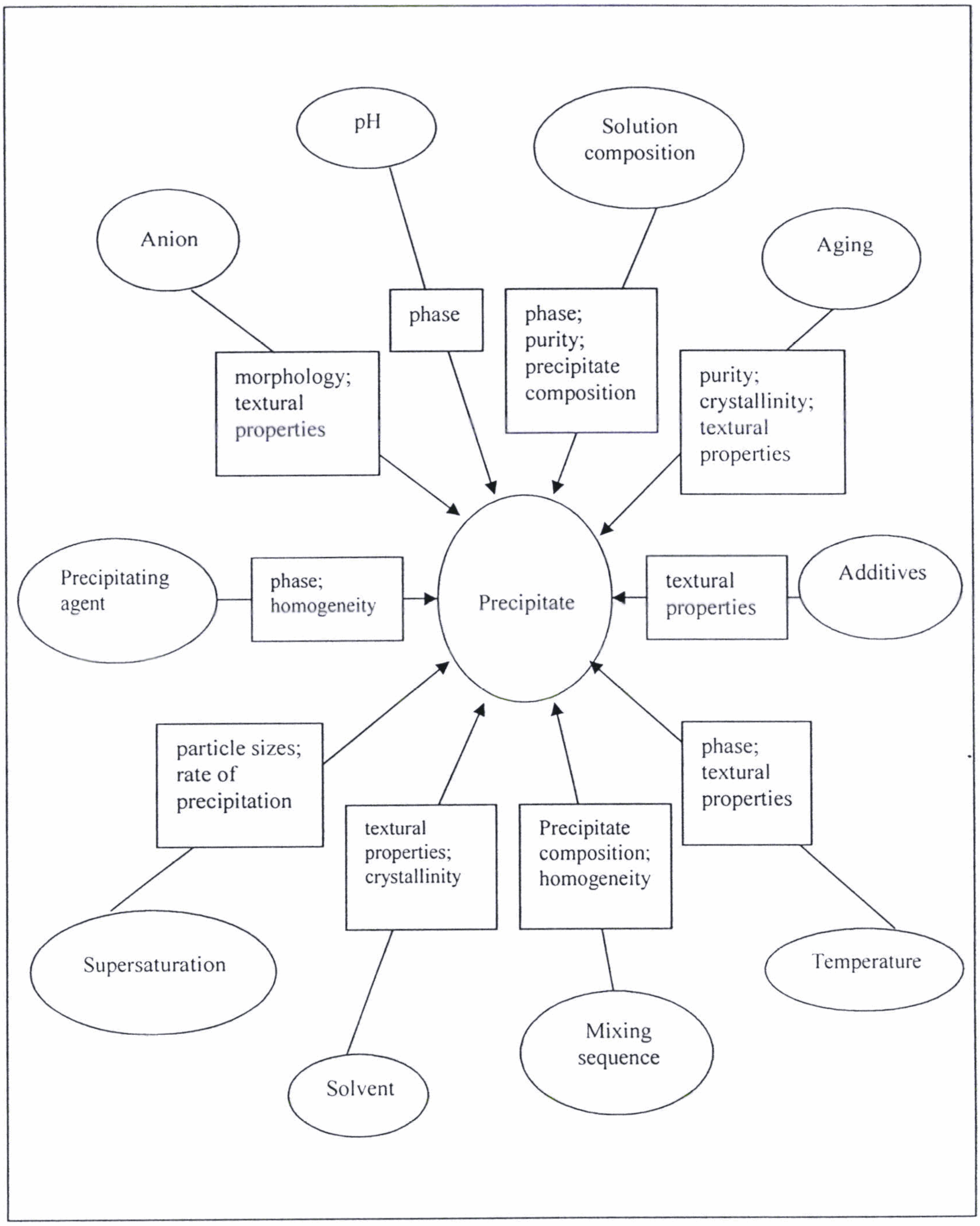

Figure 1.2: Parameters affecting the main properties of precipitated materials (Campanati *et al.*, 2003).

1.4.1 Influence of Raw Materials

Precursors are usually chosen with counter ions that can easily be decomposed to volatile products. These are preferably the nitrates of metal precursors and ammonia or sodium carbonate (Na_2CO_3) as precipitating agent. Also, oxalates have occasionally been employed. If the precipitation is carried out in the presence of ions which can be occluded, repeated washing steps are necessary, if the ions adversely affect the catalytic performance of the later catalyst. For cation Cu^{2+}, Na_2CO_3 is typically used and extensive washing of the precipitate is required to remove residual adsorbed Na^+ from the surface of the catalyst precursor (Hutchings *et al.*, 2003). Ions like chlorides or sulphates act as poisons in many catalytic reactions should be avoided in the precipitation (Schüth and Unger, 1997). For example, chlorine acts as a reversible poison for Cu catalysts and, consequently, the metal salts used in catalyst preparation must be selected with care (Hutchings *et al.*, 2003). The nature of the ions present in the precipitation solution can strongly influence the properties of the final product (Schüth and Unger, 1997).

1.4.2 Influence of Concentration and Composition

Precipitation at high concentration levels of the metal ions increases the space-time yields by decreasing the vessel volume for the same mass of precipitate. Moreover, the higher degrees of supersaturation lead to faster precipitation. Thus, plant investment is reduced. With respect to the quality of the product obtained, smaller particle sizes and higher surface areas are usually achieved at higher concentration